thus the weight-increment method cannot be expected to give a very accurate measure of the thickness of the film of oxide.

The work of Chuckerbutti ('Proc. Indian Assoc. Cult. Sci.,' vol. 7, p. 75 (1922)) is vitiated by the same error.

Prof. T. Turner has lately informed me that in the course of a research by F. B. Jenkins, carried out at Birmingham in 1920, it was shown possible to alter the colour of blued steel to purple and yellow by means of very dilute sulphuric acid. Unfortunately Jenkins's work was never published.

It would appear, therefore, that the reversed colour-changes, the existence of which Mallock regarded as essential to the interference-view, have been demonstrated independently by four different workers using four different methods.]

On the Quantum Dynamics of Degenerate Systems.

By A. M. Mosharrafa, D.Sc., Ph.D.

(Communicated by Prof. O. W. Richardson, F.R.S.—Received November 4, 1924.)

§1. It is well known that if

$$F_i = n_i h, \qquad i = 1, 2, \ldots \tag{1}$$

be a set of quantum conditions applicable to a class of dynamical systems, then F_i must satisfy the definite condition:

$$\partial F_i/\partial a = 0, \tag{2}$$

where a is a parameter, such as an external field, etc., which is allowed to undergo a slow non-systematic variation. In other words, F_i must be an "adiabatic invariant" of the class of systems. Burgers* has shown, on the basis of Newtonian dynamics, that

$$I_i = \int_0 p_i dq_i$$

fulfils this condition in the case of a conditionally periodic system of several degrees of freedom where q_i, p_i are separable Hamiltonian co-ordinates, *provided the system be non-degenerate, i.e.*, provided no relation of the form

$$\sum_i s_i^j \nu^i = 0 \tag{3}$$

* J. M. Burgers, 'Ann. d. Phys.,' vol. 52, p. 195 (1917).

exist between the frequencies ν^i, where s_i^j is an integer, positive or negative. In the case of a system of charged particles, W. Wilson* has shown that on the basis of the general theory of relativity, p_i should be replaced by π_i, where

$$\pi_i = p_i + eA_i, \tag{4}$$

e being the charge on the particle involved and A the generalised magnetic vector potential. Thus the application of the quantum conditions in the form

$$J_i = \int_0 \pi_i dq_i = n_i h, \tag{5}$$

where n_i is a positive integer (including zero) and the integration is extended from $q_i =$ minimum to $q_i =$ maximum and back to $q_i =$ minimum, can only be said to have been justified in the case of non-degenerate systems.

§2. If now we consider a degenerate configuration, we no longer find that each of the phase-integrals J_1, J_2, ..., is, in general, an adiabatic invariant. If, however, a "cyclic" co-ordinate q_s exist, such that the corresponding momentum co-ordinate π_s is independent of the variable parameter a, then the phase-integral

$$J_s = \int_0 \pi_s dq_s \tag{6}$$

will clearly be independent of a, *i.e.*, will be an adiabatic invariant. For such co-ordinates we may still write

$$J_s = n_s h, \tag{7}$$

where n_s is a positive integer. An example of such a cyclic co-ordinate is the azimuthal angle ψ about the direction of the external field in the case of the hydrogen atom. Further, it has been shown† that certain linear combinations of J_1, J_2, ..., are adiabatic invariants for degenerate systems. These are given by

$$Y_j = \sum_i r_j^i J_i, \tag{8}$$

where r_j^i is an integer, positive or negative, such that

$$\Sigma s_i^j r^i = 0 \tag{9}$$

and s_i^j is defined by (3) above. It is natural, therefore, to postulate that the quantum conditions for degenerate systems assume the form

$$Y_j = \tau_j h, \qquad j = 1, 2, \ldots \tag{10}$$

* W. Wilson, 'Roy. Soc. Proc.,' A, vol. 102, p. 478 (1922).

† 'Akad. van Wetensch. Amsterdam, Sitz.' v. 30, Dez. 1916; note, however, that we replace the co-ordinate p_i by the corresponding π_i.

where τ_j is an integer, positive or negative, together with the general conditions (7) which apply to cyclic co-ordinates whether the system be degenerate or otherwise.

§3. The application of the postulates of the previous section to a specified problem may be illustrated by an example. Taking the case of a hydrogen atom [mass of electron: m_0, charges on electron and nucleus: $(-e)$ and E respectively] in the presence of an external electric field F and referring the system to parabolic co-ordinates (ξ, η, ψ) with the origin in the nucleus and the axis of ψ in the direction of F, so that

$$q_1 = \xi, \qquad q_2 = \eta, \qquad q_3 = \psi, \tag{3.1}$$

we arrive at the well-known expression for the energy

$$W = \frac{-(2\pi eE)^2 m_0}{2(J_1+J_2+J_3)^2} - \frac{3F}{8\pi^2 m_0 E}(J_2-J_1)(J_1+J_2+J_3), \tag{3.2}$$

where both the relativity refinement and higher powers of F are neglected. We calculate the frequencies from the formula

$$\nu^i = \partial W/\partial J_i \tag{11}$$

giving:

$$\left.\begin{aligned} \nu^1 &= \frac{(2\pi eE)^2 m_0}{(J_1+J_2+J_3)^3} + \frac{3F}{8\pi^2 m_0 E}(2J_1+J_3) \\ \nu^2 &= \frac{(2\pi eE)^2 m_0}{(J_1+J_2+J_3)^3} - \frac{3F}{8\pi^2 m_0 E}(2J_2+J_3) \\ \nu^3 &= \frac{(2\pi eE)^2 m_0}{(J_1+J_2+J_3)^3} + \frac{3F}{8\pi^2 m_0 E}(J_1-J_2) \end{aligned}\right\} \tag{3.3}$$

so that

$$\nu^1 + \nu^2 - 2\nu^3 = 0. \tag{3.4}$$

This last equation corresponds to (3) above and the system is thus seen to possess a one-fold degeneracy. In order to find a set of equations corresponding to (8) we have from (9)

$$r^1 + r^2 - 2r^3 = 0 \tag{3.5}$$

giving the two independent solutions

$$\left.\begin{aligned} &r_1{}^1 = r_1{}^2 = r_1{}^3 = 1 \\ &r_2{}^1 = -1, \qquad r_2{}^2 = +1, \qquad r_2{}^3 = 0 \end{aligned}\right\} \tag{3.6}$$

whence we have the two independent invariants

$$\left.\begin{aligned} Y_1 &= J_1 + J_2 + J_3 \\ Y_2 &= J_2 - J_1 \end{aligned}\right\} \tag{3.7}$$

The hypothesis (10) now leads to the quantum conditions

$$\left.\begin{aligned} J_1 + J_2 + J_3 &= \tau_1 h \\ J_2 - J_1 &= \tau_2 h \end{aligned}\right\} \tag{3.8}$$

and, further, as J_1, J_2, J_3 are defined in such a way as to be all positive, we see that τ_1 must remain a positive integer whilst τ_2 may be either a positive or a negative integer. The co-ordinate ψ being cyclic we, moreover, have from (7)

$$J_3 = n_3 h \tag{3.9}$$

where n_3 is a positive integer subject to the condition

$$n_3 \geqslant \tau_1. \tag{3.10}$$

We see from (3.2) and (3.8) that the energy expression involves no other functions of J_1, J_2, J_3 than the two adiabatic invariants Y_1, Y_2. Thus, in calculating the *frequencies* of the light emitted, we need only consider the two quantum conditions (3.8). The *polarisation* and *intensities* of the various components, on the other hand, are governed by the azimuthal condition (3.9) which refers to the direction of the external field. Thus, following Sommerfeld* we exclude the value 0 from the possible values for J_3, since it involves a collision of the electron with the nucleus. This leads to the restriction on τ_2.

$$|\tau_2| < \tau_1. \tag{3.11}$$

In order to compare the results of our theory with the already existing Epstein-Sommerfeld theory, we have, on solving (3.8) and (3.9) for J_1, J_2, J_3:

$$\left.\begin{aligned} J_1 &= (\tau_1 - n_3 - \tau_2)\, h/2 \\ J_2 &= (\tau_1 - n_3 + \tau_2)\, h/2 \\ J_3 &= n_3 h \end{aligned}\right\} \tag{3.12}$$

This is equivalent to

$$\left.\begin{aligned} J_1 &= n_1 h \\ J_2 &= n_2 h \\ J_3 &= n_3 h \end{aligned}\right\} \tag{3.13}$$

where n_1 and n_2 (but not n_3) may simultaneously assume half-integral values. Thus if we consider the "ground orbit" of the Balmer series we have in addition to the whole-number values:

$$(n_1, n_2) = (0, 1);\ (1, 0)$$

the fractional value

$$(n_1, n_2) = (\tfrac{1}{2}, \tfrac{1}{2})$$

* 'Atomic Structure and Spectral Lines,' English Translation, p. 238 (1923).

and for the H_β orbit ($\overline{n_1 + n_2 + n_3} = 4$) we must also permit the fractional values:

$$(n_1, n_2) \text{ or } (n_2, n_1) = (\tfrac{1}{2}, 2\tfrac{1}{2}), (1\tfrac{1}{2}, 1\tfrac{1}{2}), (\tfrac{1}{2}, 1\tfrac{1}{2}), (\tfrac{1}{2}, \tfrac{1}{2})$$

and so forth.

In a previous paper* the adoption of such half-integral values has been suggested on other grounds and has been shown to account successfully for exactly those observed components of H_β which have not been explained on the Epstein-Sommerfeld theory.

§4. In the foregoing section we have neglected the relativity refinement since no system of co-ordinates has hitherto been discovered in which the variables are separable on relativistic dynamics. It is, however, noteworthy that in the case of orbits which would be circular in the absence of the external field the variables actually allow themselves to be separated if we neglect products of F and $1/c^2$, where c is the velocity of light. For such orbits we have the relation

$$\left.\begin{aligned} q_1^2 + q_2^2 &= 2r \\ &= \text{constant} + \text{terms in F} \end{aligned}\right\} \tag{4.1}$$

where r is the distance of the electron from the nucleus. The relativistic Hamiltonian equation, which may be put in the form

$$\begin{aligned} p_1^2 + p_2^2 + \left(\frac{1}{q_1^2} + \frac{1}{q_2^2}\right) p_3^2 &= 2m_0 W (q_1^2 + q_2^2) - meF (q_1^4 - q_2^4) \\ &\quad + 4m_0 eE + \frac{2r}{c^2} \{W + eE/r - eF (q_1^2 - q_2^2)/2\}^2 \end{aligned} \tag{4.2}$$

is seen to allow of separation of the variables if we neglect products of F and $1/c^2$ and thus write for the last term in view of (4·1)

$$2r_0 (W_0 + eE/r_0)^2/c^2,$$

where r_0 and W_0 are calculated in the absence of the field:

$$\left.\begin{aligned} r_0 &= (J_1 + J_2 + J_3)^2/(2\pi)^2 m_0 eE \\ W_0 &= -(2\pi eE)^2 m_0/2 (J_1 + J_2 + J_3)^2 \end{aligned}\right\} \tag{4.3}$$

This is seen to be equivalent to replacing eE by

$$\begin{aligned} eE \{1 + r_0 (W_0 + eE/r_0)^2/2eEm_0c^2\} \\ = eE \{1 + (2\pi eE)^2/8c^2 (J_1 + J_2 + J_3)^2\} \end{aligned} \tag{4.4}$$

* 'Roy. Soc. Proc.,' A, vol. 105, p. 641 (1924).

On using this result in the formula for the energy we have the relativistic expression for this class of orbits

$$W = -\frac{(2\pi eE)^2 m_0}{2(J_1+J_2+J_3)^2} - \frac{3F}{8\pi^2 m_0 E}(J_2-J_1)(J_1+J_2+J_3) - \frac{(2\pi eE)^4 m_0}{8c^2(J_1+J_2+J_3)^4} \quad (4.5)$$

and on applying the formula (11) above, we again have the relation (3.4) between the frequencies. Now, for this class of orbits it has been shown in a previous paper* that

$$J_2 - J_1 = 0. \quad (4.6)$$

It follows that of the fractional values which our non-relativistic analysis allows for the quantum numbers n_1, n_2, those for which

$$n_2 - n_1 = 0 \quad (4.7)$$

are also permissible on relativistic dynamics. Hence, the adoption of such sets of values as $(n_1, n_2) = (\frac{1}{2}, \frac{1}{2})$ or $(1\frac{1}{2}, 1\frac{1}{2})$ may be claimed to have been fully justified on theoretical grounds. The success attained by adopting such values in accounting for experimental results has already been pointed out in the paper quoted above.

§5. As a further illustration of the application of the quantum conditions (10) and (7) to degenerate systems, we consider the case of the harmonic oscillator taken by Sommerfeld† as an example. First, we consider a particle (mass $= m_0$) acted on by forces $(-k_1x_1, -k_2x_2, -k_3x_3)$ in the directions of three mutually perpendicular axes. The energy W, on neglecting the relativity refinement, is given by

$$W = \sum_i \sqrt{k_i/m_0}\, J_i/2\pi, \quad (5.1)$$

where

$$J_i = \int_0 \sqrt{\alpha_i - m_0 k_i x_i^2}\, dx_i \quad (5.2)$$

and α_1, α_2, α_3 are constants subject to the condition

$$\sum_i \alpha_i = 2m_0 W. \quad (5.3)$$

If k_1, k_2, k_3 are all different, the system is non-degenerate and the phase-integrals J_1, J_2, J_3 are adiabatic invariants, thus setting

$$J_i = n_i h. \quad (5.4)$$

Where n_i is a positive integer, we obtain

$$W = \sum_i \sqrt{k_i/m_0}\, n_i h/2\pi. \quad (5.5)$$

* A. M. Mosharrafa, *loc. cit.*, p. 645.

† *Loc. cit.*, p. 559.

Next, we consider a degenerate case of the problem by putting

$$k_1 = k_2 = k \text{ (say)}. \tag{5.6}$$

(5.1) and (5.2) now assume the forms

$$W = \frac{\sqrt{k/m_0}}{2\pi}(J_1 + J_2) + \frac{\sqrt{k_3/m_0}}{2\pi} J_3 \tag{5.1 A}$$

$$\left.\begin{aligned} J_1 &= \int_0 \sqrt{\alpha_1 - m_0 k x_1^2}\, dx_1 \\ J_2 &= \int_0 \sqrt{\alpha_2 - m_0 k x_2^2}\, dx_2 \\ J_3 &= \int_0 \sqrt{\alpha_3 - m_0 k_3 x_3^2}\, dx_3 \end{aligned}\right\} \tag{5.2 A}$$

the frequencies as given by the formula

$$\nu^i = \partial W/\partial J_i$$

conform to the relation

$$\nu^1 - \nu^2 = 0, \tag{5.7}$$

whence we have for (9)

$$r^1 - r^2 = 0 \tag{5.8}$$

and thus the adiabatic invariant corresponding to (10) is

$$Y_1 = J_1 + J_2$$

Thus we have

$$\left.\begin{aligned} J_1 + J_2 &= \tau h \\ J_3 &= n_3 h \end{aligned}\right\} \tag{5.9}$$

the last condition being clearly independent of the degenerate nature of the system. The expression for the energy is therefore

$$W = \frac{\sqrt{k/m_0}}{2\pi}\tau h + \frac{\sqrt{k_3/m_0}}{2\pi} n_3 h. \tag{5.5 A}$$

We now refer the same degenerate system to cylindrical co-ordinates (r, θ, x_3); this gives

$$W = (2J_r + J_\theta)\sqrt{k/m_0}/2\pi + \sqrt{k_3/m_0}\, J_3/2\pi \tag{5.1 B}$$

where

$$\left.\begin{aligned} J_r &= \int_0 \sqrt{[\alpha - m_0 k r^2 - \alpha'/r^2]}\, dr, \\ J_\theta &= \int_0 \sqrt{\alpha'}\, d\theta, \\ J_3 &= \int_0 \sqrt{\alpha_3 - m_0 k_3 x_3^2}\, dx_3. \end{aligned}\right\} \tag{5.2 B}$$

and the integration extends in each case, as throughout this paper, from the minimum value to the maximum value and back again to the minimum value of the independent variable involved. α, α', α_3 are constants subject to the condition

$$\alpha + \alpha_3 = 2m_0 W. \tag{5.3 B}$$

The relation between the frequencies is now

$$\nu^1 - 2\nu^2 = 0, \tag{5.7 B}$$

so that

$$r^1 - 2r^2 = 0 \tag{5.8 B}$$

and the quantum conditions are

$$\left.\begin{aligned} 2J_r + J_\theta &= \tau' h \\ J_3 &= n_3 h \\ J_\theta &= n_\theta h \end{aligned}\right\} \tag{5.9 B}$$

the last condition being in consequence of the hypothesis (10) for cyclic co-ordinates. The energy is given by

$$W = \frac{\sqrt{k/m_0}}{2\pi}\tau' h + \frac{\sqrt{k_3/m_0}}{2\pi} n_3 h. \tag{5.5 B}$$

We see that the two results (5.5 A) and (5.5 B) are in complete accord: they yield an identical set of values for the energy. In particular, we emphasise that *no discordant results concerning the orbits are yielded.* Thus one of the outstanding difficulties of the application of the quantum conditions to dynamical systems is removed.

We remark that the set of conditions (5.9 B) give for J_r half-integral multiples of h. Had we, on the other hand, integrated J_r over the complete period of the motion in the $r - \theta$ plane, namely, over twice the period of libration of r, we should have replaced $(2\ J_r)$ by (J_r) in the expression for the energy (5.1 B). This, in turn, would have involved the same substitution in (5.9 B) and thus left the final expression for the energy (5.5 B) unaltered. In fact, the limits of integration for such non-cyclic co-ordinates as r in the evaluation of the phase-integrals can in no way affect the final expression for the energy on our theory. This is especially significant in consideration of the arbitrary nature that integration limits must possess for such co-ordinates in the case of degenerate systems.

§6. Consider an f-fold degenerate system with n degrees of freedom and let m of these correspond to cyclic co-ordinates. For such a system there will be

f relations of the type (3), involving the n frequencies* $\nu^1, \nu^2, \ldots \nu^n$. Consequently there will be f equations of the type (9) involving the n integers $r^1, r^2, \ldots, r^n$. These will possess $(n-f)$ independent solutions and we shall have the $(n-f)$ quantum conditions:

$$\left.\begin{aligned} Y_1 &= r_1^1 J_1 + r_1^2 J_2 + \ldots + r_1^n J_n = \tau_1 h \\ Y_2 &= r_2^1 J_1 + r_2^2 J^2 + \ldots + r_2^n J_n = \tau_2 h \\ &\vdots \qquad\qquad \vdots \\ Y_{n-f} &= r^1{}_{n-f} J_1 + r^2{}_{n-f} J_2 + \ldots + r^n{}_{n-f} J_n = \tau_{n-f} h \end{aligned}\right\} \tag{6.1}$$

together with the m cyclic conditions

$$J_1 = s_1 h; \quad J_2 = s_2 h; \ldots J_m = s_m h. \tag{6.2}$$

If now we substitute from (6.2) in (6.1) we obtain

$$\left.\begin{aligned} r_1^{m+1} J_{m+1} + r_1^{m+2} J_{m+2} + \ldots + r_1^n J_n + \left\{ \sum_{i=1}^{i=m} s_i r_1^i - \tau_1 \right\} h = 0 \\ r_2^{m+1} J_{m+1} + r_2^{m+2} J_{m+2} + \ldots + r_2^n J_n + \left\{ \sum_{i=1}^{i=m} s_i r_2^i - \tau_2 \right\} h = 0 \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ r_{n-f}^{m+1} J_{m+1} + r_{n-f}^{m+2} J_{m+2} + \ldots + r_{n-f}^n J_n + \left\{ \sum_{i=1}^{i=m} s_i r_{n-f}^i - \tau_{n-f} \right\} h = 0 \end{aligned}\right\} \tag{6.3}$$

In the case where

$$m = f, \tag{6.4}$$

it will be possible to solve for the J's, obtaining

$$J_{m+i} = \frac{s_{m+i}}{\sigma_{m+i}} h, \qquad j = 1, 2, \ldots, \overline{n-m}. \tag{6.5}$$

where s_{m+i} involves the arbitrary integers s_i and τ_i, *but* σ_{m+i} *is a function of the fixed integers* r_j^{m+i} *alone and is therefore a fixed integer.*

It will be observed that the example considered in §4 fulfils the condition (6.4). There the fixed integer σ_{m+i} assumed the value 2 for each of the two non-cyclic co-ordinates involved. If, on the other hand,

$$m < f,$$

then it is no longer possible to assign values to each of the non-cyclic phase-integrals separately, but only to their lineal combinations $Y_1, Y_2, \ldots, Y_{n-f}$. It is these lineal combinations, as we have seen, which function in the expression for the energy.

* If any of the frequencies are not involved at all, then the corresponding co-ordinates are clearly independent of the degenerate nature of the system and the corresponding degrees of freedom may be left out of the discussion; *cf.* the co-ordinate x_3 in §5.

§7. The analysis of the preceding sections strongly suggests that the origin of the fractional numbers defining phase-integrals is to be looked for in the mechanism of degenerate systems. Thus the denominators of the fractions involved are derived in certain cases as functions of the whole numbers governing the relations between the frequencies. It is, moreover, to be remarked that as the mechanical system becomes less and less degenerate these whole-numbers [r_j^i of equation (9), §1] become larger. The whole-numbers τ_1, τ_2, etc., of the conditions (10) must therefore be assumed to increase in magnitude accordingly, if the phase-integrals are to remain finite. The quantum conditions for non-degenerate systems may therefore be looked upon as limiting forms of those for degenerate ones, where the quantum numbers τ_1, τ_2, ... increase in such a way that the right-hand side of (6.5) becomes an integral multiple of h. This transition from degenerate to non-degenerate systems does not, however, correspond on the classical side to a transition from the adiabatic invariants Y_j to the phase-integrals J_i. It is more of the nature of a sudden occurrence than a gradually approached limit.

Summary.

(1) A set of quantum restrictions is suggested for degenerate conditionally periodic systems, in the form

$$Y_j = \tau_j h,$$

where Y_j is a specified "adiabatic invariant."

(2) The conditions are applied to the case of the hydrogen atom in the presence of an external electric field and are shown to lead to the adoption of "half-integral orbits" in the Stark effect already suggested by the present writer on other grounds.

(3) A further example of the application of the conditions is discussed. It is shown that they lead to completely consistent results. In particular, *no discordant results concerning the orbits are yielded.*

(4) The relation of the hypothesis to the general question of fractional quantum numbers is pointed out. It is suggested that the origin of these fractions is to be sought in the mechanism of degenerate systems.